Polymer Journal, Vol. 28, No. 7, pp 633—636 (1996)

NOTES

Condensative Chain Polymerization. Chemoselectivity of Aryloxysilane toward Substituted Aromatic Acid Chlorides in a Model Reaction

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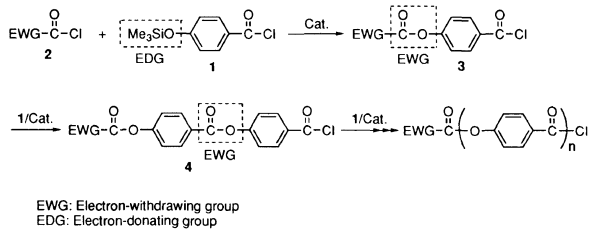
(Received November 30, 1995)

KEY WORDS Polycondensation / Chain Polymerization / Aryloxysilane / Aromatic Acid Chloride / Polyester / Siloxybenzoyl Chloride / Chemoselectivity / Fluoride Ion /

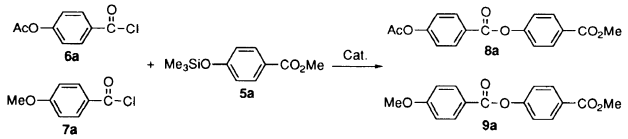
One of the exciting developments in current polymer research concerns the controlled polymerization of monomers with formation of macromolecules having a defined molecular weight and a narrow molecular weight distribution. Living polymerization techniques have been successfully utilized to synthesize such polymers based on olefinic and cyclic monomers. Since anionic, cationic, and radical propagating ends for polymerization of these monomers are generally unstable, a variety of approaches have been developed to obtain stable active chain ends for living polymerization.[1-3]

In polycondensation, reaction sites such as the carboxyl group, hydroxy group, and amino group, etc. are virtually very stable; however, the polymers of fulfilling all of the above mentioned requirements are not obtained, because polycondensation proceeds in a step-growth reaction manner. Thus, molecular weight distribution ($\bar{M}_w/\bar{M}_n$) approaches 2.0 in high conversion, although molecular weight can be controlled to some extent by change of monomer feed ratio or addition of monofunctional compounds, etc. If polycondensation proceeds in a chain-growth reaction manner from an initiator like the polymerization of vinyl monomers or cyclic monomers, polymers having a defined molecular weight and a narrow molecular weight distribution would be produced through the essentially stable propagating end groups. It occurred to us that 4-trimethylsiloxybenzoyl chloride (**1**), the typical polycondensation of that has been reported,[4] could undergo such a condensative chain polymerization by using a reactive acid chloride as an initiator. Thus, **1** would react with the reactive acid chloride **2** having an electron-withdrawing group faster than the acid chloride moiety of **1** bearing the electron-donating trimethylsiloxy group to yield the acid chloride **3** bonded to the initiator **2**. The monomer **1** would now react with **3** faster than **1** itself to yield the dimeric acid chloride **4**, because **3** has the electron-withdrawing ester linkage on the *p*-position. Growth would continue in a chain reaction manner with the conversion of the electron-donating trimethylsiloxy group of **1** to the electron-withdrawing ester linkage in the polymer (Scheme 1).

Herein we wish to report the model reactions of the above mentioned condensative chain polymerization to estimate the chemoselectivity of the monomer **1** toward the polymer end group (resulting in "chain-growth polymerization") or **1** itself (resulting in "step-growth polymerization"). Thus, we choose 4-trimethylsiloxybenzoic acid methyl ester (**5a**) as a model of the nucleophilic site of **1**, 4-acetoxybenzoyl chloride (**6a**) as a model of the propagating end, and 4-methoxybenzoyl chloride (**7a**) as a model of the electrophilic site of **1**. The chemoselectivity of **5a** toward **6a** or **7a** is studied under a variety of conditions. If the high chemoselectivity of **5a** toward **6a** is observed, **1** has the possibility of undergoing the condensative chain polymerization (Scheme 2).



Scheme 1.



Scheme 2.

EXPERIMENTAL

Preparation of Methyl 4-Trimethylsiloxybenzoate (**5a**)

The mixture of methyl *p*-hydroxybenzoate (15.22 g, 100 mmol) and 1,1,1,3,3,3-hexamethyldisilazane (HMDS) (12.7 ml, 60 mmol) was refluxed for 7 h. After removal of excess of HMDS under reduced pressure, the residue was distilled to afford **5a** (22.35 g, 100% yield): bp 81—83°C/0.6 mmHg; IR (neat) 1722, 1272, 1098, 774 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.95 (d, J=8.6 Hz, 2H), 6.86 (d, J=8.6 Hz, 2H), 3.88 (s, 3H), 0.29 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 166.8, 159.5, 131.5, 123.3, 119.7, 51.8, 0.16.

Preparation of 4-Acetoxybenzoic Acid Chloride (**6a**)

The mixture of 4-acetoxybenzoic acid (18.02 g, 100 mmol) and thionyl chloride (29 ml, 400 mmol) was refluxed for 15.5 h. After removal of excess of thionyl chloride under reduced pressure, the residue was distilled

to afford **6a** (18.97 g, 96%): bp 84—87°C/0.4 mmHg; IR (neat) 1761, 1374, 795 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.15 (d, J=8.8 Hz, 2H), 7.26 (d, J=8.8 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 168.4, 167.3, 156.2, 133.1, 130.6, 122.2, 21.1.

Preparation of 4-Methoxybenzoic Acid Chloride (**7a**)

7a was prepared from 4-methoxybenzoic acid (15.22 g, 100 mmol) and thionyl chloride (29 ml, 400 mmol) in a similar manner of **6a** (16.33 g, 96% yield): bp 66—69°C/0.35 mmHg; IR (neat) 2842, 1770, 780 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.07 (d, J=9.0 Hz, 2H), 6.96 (d, J=9.0 Hz, 2H), 3.90 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 167.1, 165.4, 134.0, 125.5, 114.3, 55.7.

Preparation of Methyl 4-(4-Acetoxybenzoyloxy)benzoate (**8a**)

Into a solution of methyl *p*-hydroxybenzoate (1.52 g, 10 mmol) and pyridine (1.2 ml, 15 mmol) in toluene (5 ml) was added a solution of **6a** (2.70 g, 15 mmol) in toluene (5 ml), and the mixture was refluxed for 19.5 h. The reaction mixture was poured into water, extracted with dichloromethane, and then washed with water. After drying over $MgSO_4$, the organic layer was concentrated and the residue was recrystallized from methanol to give **8a** (2.91 g, 93% yield): mp 119—122°C; IR (KBr) 1755, 1728, 1446, 1377, 756 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.23 (d, J=8.8 Hz, 2H), 8.12 (d, J=8.8 Hz, 2H), 7.29 (d, J=8.8 Hz, 2H), 7.26 (d, J=8.8 Hz, 2H), 3.92 (s, 3H), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 168.7, 166.3, 163.8, 155.1, 154.5, 131.9, 131.2, 127.9, 126.1, 122.0, 121.7, 52.2, 21.1.

Preparation of Methyl 4-(4-Methoxybenzoyloxy)benzoate (**9a**)

9a was prepared from methyl *p*-hydroxybenzoate (2.28 g, 15 mmol) and **7a** (3.07 g, 18 mmol) in a similar manner of **8a** and recrystallized from ethyl acetate (3.88 g, 90% yield): mp 148—152°C; IR (KBr) 2842, 1731, 1716, 759 cm^{-1}; ^1H NMR (DMSO-d_6) δ 8.08 (d, J=9.3 Hz, 2H), 8.03 (d, J=9.3 Hz, 2H), 7.39 (d, J=8.8 Hz, 2H), 7.10 (d, J=8.8 Hz, 2H), 3.88 (s, 6H); ^{13}C NMR (DMSO-d_6) δ 165.7, 164.3, 163.8, 154.7, 132.1, 130.7, 127.6, 122.0, 121.1, 114.5, 55.8, 52.0.

Preparation of Methyl 3-Methoxy-4-trimethysiloxybenzoate (**5b**)

5b was prepared from methyl 4-hydroxy-3-methoxybenzoate (5.95 g, 32.7 mmol) and HMDS (6.9 ml, 32.7 mmol) in a similar manner of **5a** (7.22 g, 87% yield): bp 95—96°C/0.6 mmHg; IR (neat) 1722, 1254, 1035 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.52—7.64 (m, 2H), 6.87 (d, J=8.3 Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 0.26 (s, 9H).

Preparation of 4-Acetoxy-3-methoxybenzoic Acid Chloride (**6b**)

Into a solution of 4-hydroxy-3-methoxybenzoic acid (16.82 g, 100 mmol) in toluene (100 ml) was added pyridine (9.7 ml, 120 mmol) and acetic anhydride (12.3 ml, 130 mmol) successively. The reaction mixture was refluxed for 11 h and poured into water, extracted with dichloromethane, and then washed with water. After drying over $MgSO_4$, the organic layer was concentrated and the residue was recrystallized from hexane–ether cosolvent to give 4-acetoxy-3-methoxybenzoic acid (9.58 g, 46% yield, mp 148—151°C). The mixture of the acetate obtained (8.41 g, 40 mmol) and thionyl chloride (10.7 ml, 160 mmol) was refluxed for 18.5 h. After removal of excess of thionyl chloride, the residue was distilled to afford **6b** (7.07 g, 77%): bp 121°C/0.8 mmHg; IR (KBr) 1758, 840, 762 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.78 (dd, J=2.4 and 8.3 Hz, 1H), 7.36 (d, J=2.4 Hz, 1H), 7.17 (d, J=8.3 Hz, 1H), 3.89 (s, 3H), 2.33 (s, 3H).

Preparation of 3,4-Dimethoxybenzoic Acid Chloride (**7b**)

7b was prepared from 3,4-dimethoxybenzoic acid (10.02 g, 55 mmol) and thionyl chloride (14.7 ml, 220 mmol) in a similar manner of **6a** (10.53 g, 96% yield): bp 108—109°C/0.9 mmHg; IR (KBr) 1767, 801, 756 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.78 (dd, J=2.4 and 8.3 Hz, 1H), 7.53 (d, J=2.4 Hz, 1H), 6.94 (d, J=8.3 Hz, 1H), 3.98 (s, 3H), 3.94 (s, 3H).

Preparation of Methyl 4-(4-Acetoxy-3-methoxybenzoyloxy)-3-methoxybenzoate (**8b**)

8b was prepared from methyl 4-hydroxy-3-methoxybenzoate (1.31 g, 7.2 mmol) and **6b** (1.45 g, 6.4 mmol) in a similar manner of **8a** and recrystallized from methanol (1.66 g, 72% yield): mp 160—163°C; IR (KBr) 1770, 1737, 1720, 789, 759 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.70—7.94 (m, 4H), 7.21 (d, J=7.6 Hz, 1H), 7.18 (d, J=8.1 Hz, 1H), 3.96 (s, 3H), 3.92 (s, 3H), 3.88 (s, 3H), 2.35 (s, 3H).

Preparation of Methyl 3-Methoxy-4-(3,4-dimethoxybenzoyloxy)benzoate (**9b**)

9b was prepared from methyl 4-hydroxy-3-methoxybenzoate (0.91 g, 5.0 mmol) and **7b** (1.20 g, 6.0 mmol) in a similar manner of **8a** and recrystallized from methanol (0.812 g, 47% yield): mp 125—129°C; IR (KBr) 1725, 777, 759 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.88 (dd, J=2.0 and 8.4 Hz, 1H), 7.64—7.78 (m, 3H), 7.22 (d, J=7.8 Hz, 1H), 6.96 (d, J=8.4 Hz, 1H), 3.97 (s, 3H), 3.96 (s, 3H), 3.93 (s, 3H), 3.88 (s, 3H).

Model Reaction

Catalyst (10 mol%) was dried at 250°C (in the case of metal halides) or 90°C (in the case of ammonium halides) under vacuum in a round flask, and cooled at room temperature under argon atmosphere. Into the flask was added a solution of 18-crown-6 (0.199 g, 10 mol%) in solvent (1 ml), a solution of **6** (1 mmol) and **7** (1 mmol) in solvent (1 ml), and a solution of **5** (1 mmol) and an internal standard (*ca.* 0.2—0.4 mmol) in solvent (1 ml), successively. After stirring for 48 h, the conversion of **5** and the yields of **8** and **9** were determined by gas chromatography, respectively.

RESULTS AND DISCUSSION

The model reactions of **5a** with equimolar **6a** and **7a** were carried out with a catalytic amount of chloride or fluoride ion under various conditions, and the conversions of **5a**, the yields and product ratios of **8a** and **9a** were determined by a gas chromatography (GC).

The reaction catalyst was first studied (Table I). Since

Table I. Effect of catalysts on the reaction of **5a** with **6a** or **7a**[a]

Catalyst[b]	Concentration of **5a**	Conversion[c]	Yield[c]	Mole ratio[c]
	mol l^{-1}	%	%	**8a**:**9a**
BTEA-Cl[d]	0.33	14	13	75:25
KCl/18-C-6[e]	0.33	12	11	83:17
KF/18-C-6	0.67	25	25	74:26
	0.33	21	20	84:16
	0.17	18	15	90:10

[a] The reaction was carried out in CH_2Cl_2 ($[\mathbf{5a}]_0=[\mathbf{6a}]_0=[\mathbf{7a}]_0$) at 25°C for 48 h. [b] 10 mol% to **5a**. [c] Determined by GC. [d] Benzyltriethylammonium chloride. [e] 18-Crown-6.

Table II. Solvent effect on the reaction of **5a** with **6a** or **7a**[a]

Solvent[b]	Temp	Conversion[c]	Yield[c]	Mole ratio[c]
	°C	%	%	**8a**:**9a**
CH_2Cl_2	25	21	20	84:16
	60	33	28	68:32
Ph-CH_3	25	14	11	92:8
	60	34	33	76:24
	100	49	47	61:39
DME[d]	0	18	16	84:16
	25	20	20	89:11
	60	48	44	77:23
	80	35	34	78:22
	100	70	57	64:36
THF	25	20	20	88:12
CH_3CN	25	15	15	80:20
DMF	25	100	31	69:31

[a] The reaction was carried out with 10 mol% of KF/18-C-6 for 48 h. [b] $[\mathbf{5a}]_0=[\mathbf{6a}]_0=[\mathbf{7a}]_0=0.33$ mol l^{-1}. [c] Determined by GC. [d] 1,2-Dimethoxyethane.

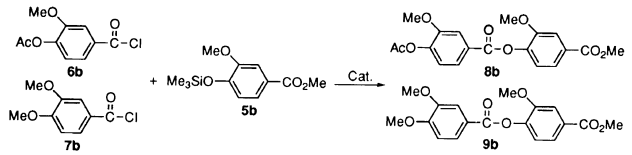
benzyltriethylammonium chloride (BTEA-Cl) has been reported to be effective for the polymerization of **1**,[5] the reaction was carried out with BTEA-Cl in dichloromethane, resulting in the preferential production of **8a** that was formed by the reaction of **5a** with the acetoxy-substituted acid chloride **6a**. When KCl was used with equimolar 18-crown-6 (18-C-6) instead of BTEA-Cl, the product mol ration **8a**/**9a** increased in spite of a slight decrease of the conversion. Furthermore, an increased conversion was attained by KF/18-C-6 system, maintaining the preferential formation of **8a**. In the reaction with KF/18-C-6 system, the ratio **8a**/**9a** was effected on the concentration of reactants: it increased with decreasing the concentration, especially increased up to 90/10 in the concentration of **5a** being 0.17 mol l^{-1}.

The reaction was next carried out with KF/18-C-6 system in a variety of solvents (Table II). The ratios **8a**/**9a** were higher in nonpolar solvents such as toluene or ethers than in polar solvents such as acetonitrile or *N*,*N*-dimethylformamide (DMF), especially in toluene the ratios **8a**/**9a** was the highest resulting in 92/8. In DMF the yield was 31% despite 100% conversion, implying that the reaction of acid chloride **6a** and **7a** with DMF (Vilsmeier reaction[6]) may take place faster than the desired reaction of **5a** with **6a** or **7a**. Since the conversions of **5a** were low at 25°C in nonpolar solvents, the reactions were then carried out at temperature above 60°C. In any solvents, dichloromethane, toluene, and 1,2-dimethoxyethane (DME), the conversions and yields increased with temperature; however, the important ratios **8a**/**9a** decreased with temperature. Additionally, the conversions were in fair agreement with the yields in toluene, implying that the reaction in toluene proceeded with little side reactions even at increased temperature.

Table III. Effect of Lewis acid[a]

Lewis acid[b]	Conversion[c]	Yield[c]	Mole ratio[c]
	%	%	**8a**:**9a**
$Eu(fod)_3$[d]	19	9	80:20
$ZnCl_2$	100	85	15:85
Ph_3CClO_4	100	89	4:96

[a] The reaction was carried out with 10 mol% of KF/18-C-6 in CH_2Cl_2 ($[\mathbf{5a}]_0=[\mathbf{6a}]_0=[\mathbf{7a}]_0=0.33$ mol l^{-1}) at 25°C for 48 h. [b] 20 mol% to **5a**. [c] Determined by GC. [d] Europium trisheptafluorobutanoylpivaloylmethanate.



Scheme 3.

Table IV. Reaction of **5b** with **6b** or **7b**[a]

Solvent[b]	Conversion[c]	Yield[c]	Mole ratio[c]
	%	%	**8b**:**9b**
THF	35	29	46:54
CH_3CN	33	29	45:55

[a] The reaction was carried out with 10 mol% of KF/18-C-6 at 25°C for 48 h. [b] $[\mathbf{5b}]_0=[\mathbf{6b}]_0=[\mathbf{7b}]_0=0.33$ mol l^{-1}. [c] Determined by GC.

The aryloxysilane **5a** was allowed to react with **6a** or **7a** also in the presence of Lewis acid that is expected to activate **6a** by virtue of the coordination to the acetoxy group of **6a** to increase the conversion and ratio **8a**/**9a** (Table III). The result with $Eu(fod)_3$ was not appreciably different from that without it. When 20 mol% of $ZnCl_2$ or Ph_3CClO_4 was added into the reaction mixture, the yields were dramatically increased, but **9a** was predominately formed, contrary to the reaction without Lewis acid. The observed reverse results are ascribed to the coordination of these Lewis acids to the acyl chloride moiety of **7a** that gives stabler acylinium ion compared to **6a** owing to the electron-donating methoxy group.

The reactions of 3-methoxy-substituted analogs, **5b**, **6b**, and **7b** were also carried out with KF/18-C-6 in tetrahydrofuran (THF) and acetonitrile (Scheme 3, Table IV). The methoxy-substituted aryloxysilane **5b** reacted with the acetoxy-substituted **6b** and with the methoxy-substituted **7b** nonselectively to yield **8b** and **9b** with almost 1:1 either in THF or in acetonitrile. This implies that the analogs of **1** substituted with electron-donating groups hardly undergo the condensative chain polymerization.

In summary, the observed high chemoselectivity of **5a** toward the acid chloride **6a** having the ester moiety at the *p*-position indicates that the monomer **1** has the possibility of undergoing the condensative chain po-

lymerization. However, the polymerization of **1** proceeds accompanying precipitation of the polymer, and whether the condensative chain polymerization takes place or not is not evaluated. Consequently, the condensative chain polymerization should be studied by using the derivatives of **1** yielding soluble polymers. Experiments along these lines as well as design of other types of monomers undergoing the condensative chain polymerization are in progress.

Acknowledgments. This work was supported in part by a Grant-in-Aid for Scientific Research (No. 07805084) from the Ministry of Education, Science, and Culture of Japan, and by Kanagawa Academy of Science and Technology Research Grants (No. 951114).

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